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BODIPY-4H-Pyran Hybrids Synthesis

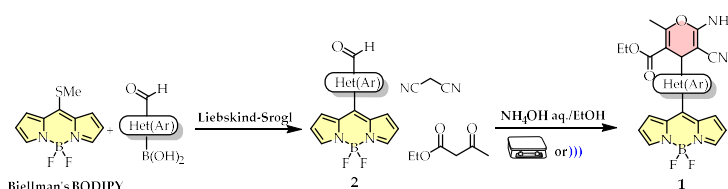
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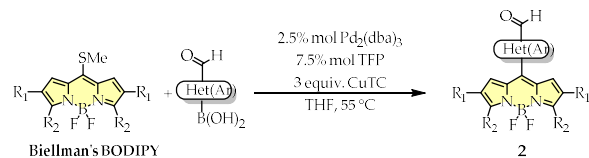
STATEMENT

One-pot multicomponent reactions (MCRs) are efficient chemical transformations with high atom economy and a rapidly manner for molecular complexity targets synthesis. In that sense, is well known base-catalyzed reaction of an aldehyde, malononitrile and ethyl acetoacetate for synthesis of 4H-pyran (1). Incorporation of fluorescent scaffold to molecular complex molecule increase it value and application possibilities. Attending this precepts we contribute with a synthetic procedure for BODIPY-4H-Pyran hybrids synthesis through MCR using formyl-containing BODIPYs (2) obtained by Pd-catalyzed Liebskind-Srogl (LSCC) and Suzuki-Miyaura (SMCC) cross couplings. Finally, products 1 were obtained by conventional heating and some of same products by reduced waste ultrasound assisted procedure.



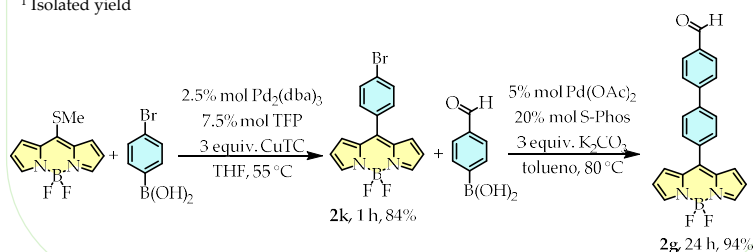
SCREENING OF MCR

LSCC FOR ALDEHYDE SYNTHESIS



compound	Het(Ar)	R ₁ , R ₂	time	yield(%) ¹
2a		-H, -H	0.5 h	75
2b		-H, -H	0.5 h	98
2c		-H, -H	0.5 h	80
2d		-H, -H	1 h	72
2e		-H, -H	0.5 h	86
2f		-H, -H	4 h	71
2h		-H, -CH ₃	1 h	68
2i		-Br, -CH ₃	1 h	67
2j		-H, -CH ₃	6 h	64

¹ Isolated yield

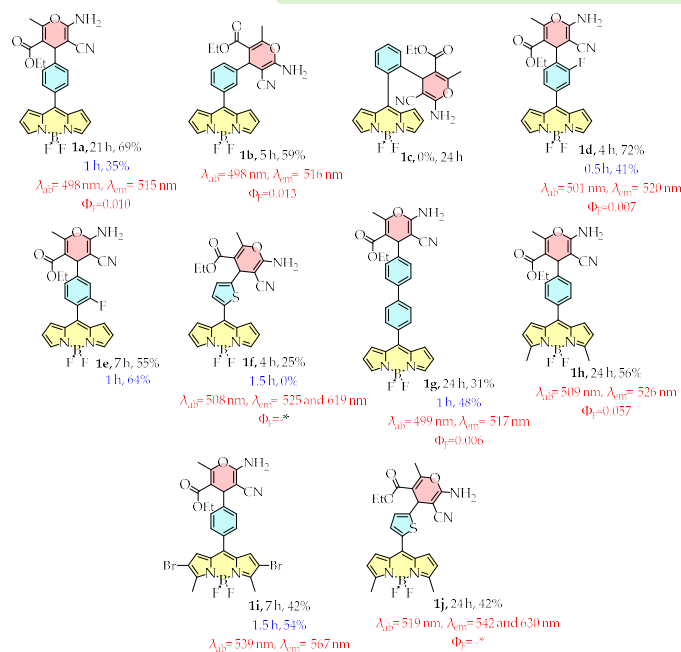


entry	solvent	temperature	time	Yield (%) ¹
1	EtOH/water	r.t.	4 h	72 (83) ²
2	EtOH/water	reflux	4 h	70

¹ Isolated yield

² Conversion determined by ¹H NMR.

BODIPY-4H-PYRAN HYBRIDS



Method A: 3 (1 equiv.), malononitrile (1 equiv.), ethyl acetoacetate (1 equiv.), NH₄OH (1 equiv.), ethanol, room temperature. **Method B:** 3 (1 equiv.), malononitrile (1 equiv.), ethyl acetoacetate (1 equiv.), NH₄OH (1 equiv.), ethanol, sonication (42 kHz). **Optical properties:** λ_{ab} = absorption maximum, λ_{em} = emission maximum, Φ_f = fluorescence quantum yield estimated in MeOH using the parent Borondipyrromethene (Φ_f = 80.8 % in EtOAc) as standard.

CONCLUSIONS

It was obtained new highly functionalized bioconjugates composed by BODIPY and 4H-pyran by MCR catalyzed by aqueous NH₄OH, malononitrile, ethyl acetoacetate and formyl-containing BODIPYs through two equipareble methods. Method A by conventional heating and method B by greener procedure as ultrasonic activation.

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